

Chemical Signature of the Superconducting Phase in the Nd-Ce-Cu-O System

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The electron-doped material $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ becomes superconducting with a Ce^{4+} composition around 0.16, but only after removal of a minuscule amount of extraneous oxygen. This enigmatic behavior was addressed here. A small fraction of copper in the CuO_2 planes of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ was substituted by cobalt-57, which serves as a microprobe of the chemical environment. Deoxygenation brought about little change in the Mössbauer spectra both above and below the optimal superconducting concentration; however, for $x = 0.16$ a change was observed. In the latter, a major fraction of the magnetically split, five-coordinate species showed itself as a paramagnetically relaxed doublet upon deoxygenation. The abundance of the paramagnetically relaxed species corresponds closely to the diamagnetic volume fraction and thus provides a microscopic signature of the superconducting phase.

In the insulating parent compound Nd_2CuO_4 , the Cu ions in the CuO_2 planes are antiferromagnetically ordered; when Ce^{4+} ions are substituted for Nd^{3+} , the resultant electron-doped material can become superconducting in a narrow concentration range of Ce of approximately 0.16. The electron-doped systems differ from their hole-doped analogs (for example, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$) in several respects (1, 2). For instance, in the former the Cu ions in the CuO_2 planes ideally have four O^{2-} nearest neighbors in a square-planar configuration; in the latter they have an octahedral arrangement. The most interesting difference in their behavior is that the as-prepared electron-doped material is not superconducting but requires the removal of about 0.02 O atoms per formula unit for the onset of superconductivity. This remarkable behavior has attracted considerable attention (1, 2). It is generally believed that there is a small amount of extraneous oxygen present in the positions apical with respect to the Cu ions (3). Emission Mössbauer spectroscopy provides a valuable tool to probe the microenvironment of the Cu sites because it is much more sensitive than the absorption mode (4, 5) and requires a minimal perturbation of the system by substitution of only 20 to 30 parts per million of ^{57}Co for Cu (5). We report here the results of studies on oxygenated and deoxygenated $\text{Nd}_{2-x}\text{Ce}_x\text{Cu}^{(57)\text{Co}}\text{O}_4$, where $x = 0.00$,

0.14, 0.16, and 0.18. A direct correlation between the abundance of the five-coordinate species doublet and the superconducting volume fraction was observed.

Samples of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ were doped with ^{57}Co by allowing the carrier-free ^{57}Co activity to diffuse into the material at about 1000°C in an O_2 atmosphere. Deoxygenation of samples was performed under Ar flow at 850° to 875°C for 20 to 30 hours. The cycle of oxygenation and deoxygenation was repeated to check the reproducibility of experimental observations, which ensures that ^{57}Co is sitting at the appropriate site or sites (5).

Several trial and error computer fits of the Mössbauer spectra measured at different temperatures led to a self-consistent picture. Two species were generally present that can perhaps be assigned to ^{57}Co with the five and six O^{2-} atom neighbors designated as B and C, respectively. The sites were assigned on the basis of the Mössbauer parameters, the one with six oxygen neighbors having a smaller isomer shift and quadrupole splitting. However, our interpretation and conclusions are not dependent on site assignments. The four-coordinate species A was not observed with the conventional procedure for deoxygenation.

We have shown that all oxygenated as well as deoxygenated $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ materials, including the superconducting compound with $x = 0.16$, have a fraction of coexisting microscopic spin clusters of variable size centered around $100 \text{ \AA}$ (6). In the spin clusters, the two-dimensional magnetic order attributable to Cu^{2+} - Cu^{2+} exchange interaction is very strong. Consequently, species B and C manifest themselves as a simple quadrupole split doublet only at temperatures above 500 K. At lower temperatures, the magnetically split sextet associated

with species C coexists with its corresponding quadrupole split doublet (Fig. 1). This is characteristic of the superparamagnetic behavior of small magnetic particles and clusters with a size distribution (6, 7). At any temperature, the thermal energy is adequate to flip the magnetization vectors of the smaller spin clusters at a rate faster than the Larmor frequency of daughter-excited ^{57}Fe ($\sim 10^8 \text{ s}^{-1}$), resulting in net zero field at the nuclei. These small clusters exhibit a superparamagnetically relaxed spectrum consisting of a quadrupole split doublet. Larger spin clusters have slower rates of flipping, and the ^{57}Fe nuclei experience an effective magnetic field. Consequently, they exhibit a magnetically split, six-line Mössbauer spectrum. Spin clusters of intermediate size with rates of flipping comparable to the Larmor frequency exhibit a more complicated spectrum. The superparamagnetically relaxed doublets grow at the expense of the sextets with an increase in temperature (Fig. 1).

The observed Mössbauer spectra were quite complex. However, the main features of the spectra are fairly well described by the two-level relaxation fitting procedure of Wickman *et al.* (8), as modified to take into account the superparamagnetic behavior. The relative abundances of species B and C were estimated by a self-consistent computer analysis of the spectra at 80 K (at velocity ranges of $\pm 15 \text{ mm s}^{-1}$ and $\pm 3 \text{ mm s}^{-1}$) and at 550 K (only in the smaller velocity span). The estimated error in the abundances does not exceed $\pm 10\%$.

With regard to the role of oxygen in the manifestation of superconductivity in the $\text{Nd}_{1.84}\text{Ce}_{0.16}\text{CuO}_4$ materials, the proposed presence of extraneous oxygen in the apical positions had escaped detection in earlier x-ray and neutron diffraction studies (9, 10).

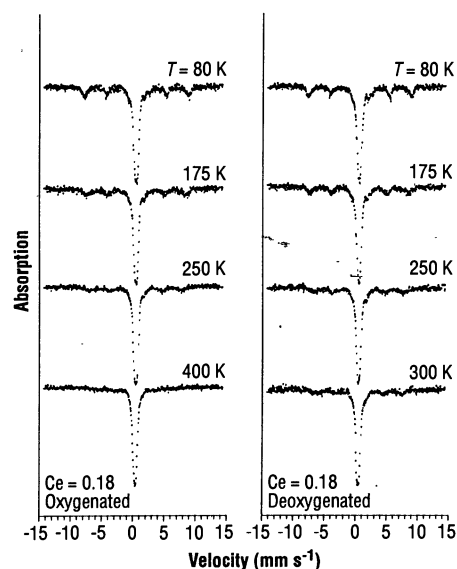


Fig. 1. Mössbauer spectra of $\text{Nd}_{1.82}\text{Ce}_{0.18}\text{Cu}^{(57)\text{Co}}\text{O}_4$ ceramic at different temperatures.

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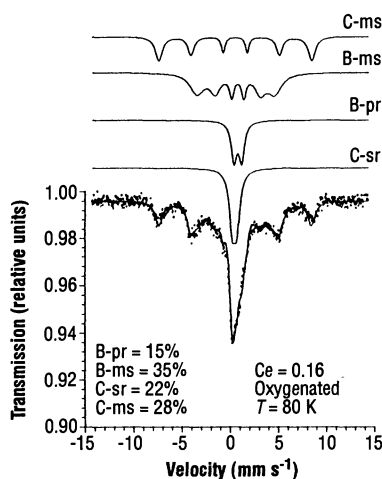


Fig. 2. Computer fit of oxygenated $\text{Nd}_{1.84}\text{Ce}_{0.16}\text{Cu}^{(57)\text{Co}}\text{O}_4$ ceramic at 80 K. Shown are magnetically split (ms), superparamagnetically relaxed (sr), and paramagnetically relaxed (pr) species B and C.

However, a single crystal neutron diffraction study of Ce-free Nd_2CuO_4 recently showed detection of nonlattice O at the level of 0.1 per unit formula at the apical sites (11). Upon deoxygenation of the crystal, this value decreases to 0.04. It is not possible to extrapolate this behavior to Ce-doped compounds. Indeed, it has been reported that the loss of O during deoxygenation decreases appreciably with an increase in Ce concentration and is about 0.02 per unit formula for a Ce composition of 0.16 (3, 12).

The Mössbauer probe ^{57}Co (^{57}Fe) can readily detect the presence of apical O^{2-} through formation of five- and six-coordinate species, as shown for the Cu-O chains in Y-Ba-Cu-O compounds (4, 5). Because ^{57}Co creates its own microenvironment by attaching apical O^{2-} , it may not quantita-

tively mimic the microenvironment of the neighboring Cu atoms. However, it has been demonstrated that the dynamics of the Cu-O chain and the changes in electron density as a result of deoxygenation can be faithfully sensed by the Mössbauer probe (5).

In our study here, the six-coordinate species C is present only in an oxygen-rich, antiferromagnetically ordered phase. Its abundance remains practically unchanged after a "conventional" deoxygenation procedure. However, the presence of oxygen reduces the size of spin clusters and induces superparamagnetism (6) (Figs. 2 and 3). We observe that, in the materials with optimal Ce concentrations, the five-coordinate species B is indicative of a potentially superconducting phase. The presence of a minuscule amount of oxygen results in the localization of the electrons donated by Ce^{3+} ions and produces spin clusters with quasi-static magnetic order in the Cu-O plane (6, 13). Therefore, species B in the oxygenated $\text{Nd}_{1.84}\text{Ce}_{0.16}\text{Cu}^{(57)\text{Co}}\text{O}_4$ material is observed as a sextet at 80 K, with the rate of magnetic fluctuations being much slower than 10^8 s^{-1} (Fig. 2). There is a change upon deoxygenation: the magnetically split species B relaxes to a doublet, which is a signature of the superconducting phase (Fig. 3). The Mössbauer spectrum of the Ce-rich compound $\text{Nd}_{1.82}\text{Ce}_{0.18}\text{Cu}^{(57)\text{Co}}\text{O}_4$ does not change upon deoxygenation (Figs. 1 and 3), which shows that the extraneous oxygen is rather tenaciously bound. This in turn shows how increased Ce concentration cannot produce superconductivity by partially nullifying the influence of extraneous oxygen. For $\text{Nd}_{1.86}\text{Ce}_{0.14}\text{Cu}^{(57)\text{Co}}\text{O}_4$, the abundance of the relaxed doublet B increases from about 9% to 14% during deoxygenation (Fig. 3). Thus, the behavior of the bulk supercon-

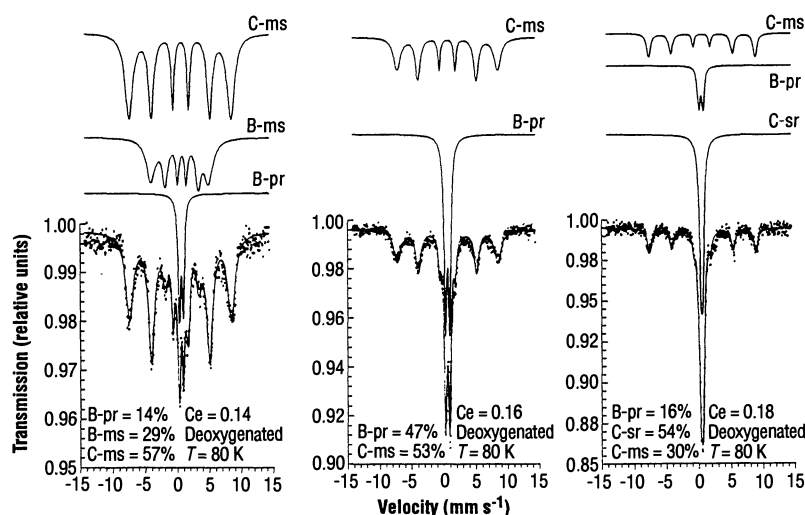


Fig. 3. Computer fit of deoxygenated $\text{Nd}_{2-x}\text{Ce}_x\text{Cu}^{(57)\text{Co}}\text{O}_4$ ceramic with $x = 0.14, 0.16$, and 0.18 . Shown are magnetically split (ms), superparamagnetically relaxed (sr), and paramagnetically relaxed (pr) species B and C.

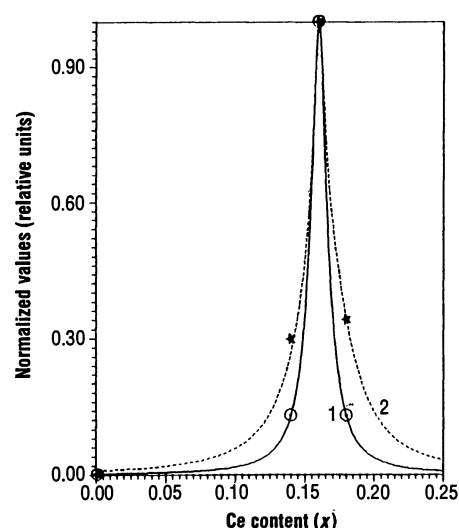


Fig. 4. Plot of diamagnetic shielding at 8 Oe (curve 1) and abundance of the paramagnetically relaxed B doublet (curve 2) as a function of Ce content. All values are normalized to those of the sample with a Ce composition of 0.16.

ductor $\text{Nd}_{1.84}\text{Ce}_{0.16}\text{Cu}^{(57)\text{Co}}\text{O}_4$ contrasts sharply with that of the rest of the nonsuperconducting compounds (Figs. 2 and 3). The relative abundance of the relaxed B doublet mirrors the superconductivity volume fraction determined from magnetic susceptibility measurements and should be considered a fingerprint of the superconducting phase (Fig. 4).

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